



NIST Combinatorial Methods Center

FOCUSED PROJECTS NON-PROPRIETARY RESEARCH AGREEMENT APPENDIX A – INTEGRATION OF MODULAR MEASUREMENT PLATFORM FOR HIGH THROUGHPUT ANALYSIS OF POLYMER SOLUTIONS AND BLENDS

Article 1. INTRODUCTION

Development of advanced formulations in the coatings and surfactant industries requires the exploration of a multi-parameter space that includes varying amounts of key components and appropriate processing conditions, and correlating these to final product properties.¹ Finding new formulations and processing conditions for an application, or fine-tuning an existing system, requires extensive sample preparation and testing. For polymer solutions and polymer blends to realize their full market potential in a cost effective manner, new high-throughput technologies in sample preparation and analysis are needed. The thin film technologies developed by the NCMC, along with new initiatives in microfluidics for polymer formulations, are promising routes for development of new integrated measurement technologies that provide rapid development and cost effectiveness despite the complex, multi-parameter space of the polymeric formulations.

Polymer solutions and polymer blends are widely used by the coatings, detergent and personal care industries in order to obtain a wide range of final properties. This fine-tuning is obtainable due to the dispersion and synergy of different component polymers and stabilizers (e.g., surfactants) and other property modifier additives. Polymer blending provides a convenient combination of individual homopolymer characteristics, which is often non-linear in composition, and therefore yields a wide range of enhanced properties without the averaging effects seen in statistical copolymers. The ability to tune a material for a particular application using polymer solutions and/or blends comes at the cost of substantial experimental effort and reliance on empirical models and experience. Application of combinatorial methods to formulation science is a facile way to address these problems.

Recently the NCMC has undertaken initiatives to develop modular, fluidics-based techniques for polymer formulations. These new techniques include: 1) Multi component mixing and generation of combinatorial solution and blend libraries; 2) Measurement of viscosity using a capillary fluidics-based viscometer and rheology (including complex viscosity) using a dynamic mini-rheometer; 3) Light scattering on a fluidics chip. Additionally, the NCMC has already developed and published techniques in thin film formation and metrology.² These methodologies will be used in an integrated form and tailored to select model-solution studies of relevance to the NCMC partners. The resulting data will be processed and managed using the NCMC informatics database.

Each of these developing technologies will be used and tailored considering the model system chosen and then integrated into a measurement platform for model coatings and surface-active agents.

Article 2. BACKGROUND

Thin film libraries and metrology

The NCMC has demonstrated expertise in the creation of thickness, composition, and thermal gradient libraries of thin films.² We have demonstrated combinatorial measurements of morphology, surface energy, modulus,³ and adhesion⁴ of these thin-film libraries. More information and relevant publications are available through the NCMC web page.⁵

Rapid prototyping of fluidic devices and multi-component mixing

We have recently developed a prototyping technique for the fabrication of fluidic devices in a polymeric matrix.⁶ The method employs contact lithography and a UV-curable adhesive and is capable of producing features with accurately controlled vertical (from 100s μm to millimeters) and lateral dimensions (from 10s μm and above). These features challenge conventional photolithography capabilities and are particularly suited for millifluidic research. Moreover, the devices can be made impervious to a range of organic solvents, a requirement for most polymer formulations studies. In addition, the technique is inherently fast and devices can be produced and rapidly, allowing for multiple iterations in design.

We have demonstrated and validated this application of microfluidics with a study of polymer blend phase behavior. Preparation of a combinatorial library of a binary mixture was performed using several syringe pumps, XYZ motion stages and controllers, and a desktop computer with home-developed software to control the system.

Millifluidics viscosity chip

A simple capillary viscometer has been fabricated using our rapid lithography technique mentioned above. The principle of operation is simple and works well with Newtonian fluids. The fluid velocity through a channel of known dimensions is measured for a given pressure drop and the viscosity is then calculated. For a cylindrical channel, the well-known equation for a capillary viscometer is used:

$$\eta = \frac{\pi R^4 \Delta P}{8QL}$$

where R is the radius of the capillary, ΔP is the pressure drop, Q is the volumetric flow rate, and L is the length of the capillary. The advantage of the capillary viscometer is its ease of use and the straightforward calculation of the apparent viscosity.

Mini, magnetic field driven combi-rheometer

Polymer formulations and blends are complicated, often non-Newtonian, fluids. This requires the ability to make measurements of viscosity at different shear rates, and preferably to measure dynamic properties such as relaxation/compliance, complex viscosity, and complex modulus. These requirements have led to our development of a dynamic rheometer capable of measuring the properties of multiple samples. A prototype rheometer has been developed which uses magnetic fields in a two axis Helmholtz coil to provide a uniform shear stress across four samples. The device is a stress-controlled rheometer using either a Couette or disk geometry.

Approach

Our new millifluidics approach to investigating the issues relevant to polymer solutions will be adapted to an integrated modular platform suitable for flow coating capabilities for polymer blend coatings. The technical approach will involve the following steps:

1. Optimize existing library generation methods for identified parameters. This includes utilizing conventional pumps for inducting pre-mixed solutions with varying polymer composition, and controlling formulation components and temperature then flowing polymer solutions through fluidic channels custom designed by rapid prototyping methods for solution property measurements. Adaptation of knife blade draw techniques on motorized stages and open channel architecture at the exit of the millifluidic channels can be used to generate polymer blend coatings.
2. Integrate currently available techniques to measure and map properties of interest (mechanical properties, morphology, optical clarity, etc.).
3. Demonstrate informatics feedback with respect to each aspect of the overall system (e.g., composition, mixing, rheology, light scattering, and select end properties).

References:

- ¹R. Dagani, "Tapping into NIST's combi expertise," Chem. & Eng. News **80**, 58-60 (2002).
²J. C. Meredith, A. Karim, E. J. Amis, "High-throughput measurement of polymer blend phase behavior," Macromolecules **33**, 5760-5762 (2000); and J. C. Meredith, A. P. Smith, A. Karim, E. J. Amis, "High-throughput measurement of polymer blend phase behavior," Macromolecules **33**, 9747- (2000)

³C.M. Stafford, C. Harrison, A. Karim, E. J. Amis, “Measuring modulus of gradient polymer films by strain-induced buckling instabilities,” ACS Polymer Preprints **43**, 1335 (2002).

⁴A. J. Crosby, A. Karim, E. J. Amis, “Combinatorial investigations of interfacial failure,” J. Polym. Sci. Polm. Phys. **41**, 883-891 (2003).

⁵<http://polymers.msel.nist.gov/combi/index.html>

⁶C. Harrison, J. T. Cabral, C. M. Stafford, E. J. Amis, A. Karim, “A rapid prototyping technique for fabrication of solvent-resistant structures,” Lab on a Chip J., submitted (2003).

Article 4. **COLLABORATION AND DISSEMINATION**

A meeting will be held six weeks after the formal launch of the project as well as at six-month intervals for the duration of the project. Quarterly reports will be submitted to the members with updates more frequently via conference calls and other postings. In order to facilitate the collaboration, specifications for methods, instruments, programs, data analysis, and other aspects of this work will be available to members during the course of the project. A summary report will be provided within two months of the end of the project. The NCMC labs will be open to prearranged visits from member scientists interested in hands-on participation in method development.

As with base level membership in the NCMC, all of the research carried out in the Focused Project is non-proprietary and is intended for publication in the public domain. No proprietary information or materials will be solicited or accepted by NIST from member organizations. The scope of the work by NIST included in this focused project is limited as described in Article 5 below.

Article 5. **PROJECT MILESTONES**

5.1 **First year:**

- 5.1.1 Select suitable model polymer solution and polymer blend system and define parameters, variables, etc. of interest to the project team.
- 5.1.2 Develop strategy to tailor investigation of the model systems using millifluidic and blend film coating techniques including prototype development, library generation, and analysis.
- 5.1.3 Conduct preliminary tests on a selected model polymer formulation and blend film system.

5.2 **Second year**

- 5.2.1 Test model systems using the tailored, integrated prototype measurement platform. Issues in library generation, high-throughput measurement, and analysis will be considered.
- 5.2.2 Integrate the above system into the NCMC informatics database.
- 5.2.3 Allow focused project members to investigate a suitable non-proprietary commercial solution or blend system to study cause effect relationships between parameters and performance using the integrated system developed and provide feedback for optimization.

Article 6. **FINANCIAL OBLIGATION**

Member’s project fees payable to NIST are set at \$20,000 per year.